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Preparation and Nonlinear Optical Properties of Au Colloid

ZHAO Chong-Jun(赵崇军)[1], QU Shi-Liang(曲士良)[1], GAO Ya-Chen(高亚臣)[2], SONG Ying-Lin(宋瑛林)[2], QIU Jian-Rong(邱建荣)[1], ZHU Cong-Shan(朱从善)[1]

[1]*Photon Craft Project, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences and Japan Science and Technology Corporation, Shanghai 201800*

[2]*Department of Physics, Harbin Institute of Technology, Harbin 150001*

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Colloidal Au less than 20 nm was prepared in an aqueous solution of $HAuCl_4$ by irradiation with a near-infrared femtosecond laser. The absorption peak around 526 nm in the absorption spectra and the peaks $2\theta = 38.3^\circ$ and $2\theta = 24^\circ$ in the x-ray diffraction (XRD) pattern indicated the formation of Au colloid. Nonlinear optical properties of Au colloid were investigated by using the Z-scan technique with 8 ns pulses at 532 nm. The transition characteristics from self-defocusing to self-focusing and from saturable absorption (SA) to reverse saturable absorption (RSA) were observed for the Au colloid.

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Metal nanoparticles, especially noble metal including Au, Ag, Pt and Pd, have been used in catalysis, nonlinear optics, electronic devices, material sciences and other fields.[1−5] In particular, Au colloid has been extensively studied because of its nonlinear optical properties and convenient operating wavelength close to the second harmonic of Nd:YAG laser. Up to now, colloidal Au has been prepared by a wide variety of fabrication methods, e.g., radiolysis, ultraviolet photochemical and chemical reduction.[6−8] However, there is no report of photoinduced formation by a near-infrared light to the best of our knowledge.

In this Letter, a Ti: sapphire femtosecond laser at 800 nm was used to prepare Au colloid in a 5-mM $HAuCl_4$ aqueous solution. Nonlinear optical properties of colloidal Au were studied by using the Z-scan technique. The mechanisms of transitions of the nonlinear absorption and refraction were analysed.

$HAuCl_4$ was dissolved in the mixture of twice-distilled water and ethanol at the ratio of 4:1 in volume, and concentration of $HAuCl_4$ was 5 mM. In the laser-irradiation experiment, 2 ml of the solution was introduced in a rectangular quartz vessel of $0.5 \times 1 \times 4\,cm^3$ and irradiated by the fundamental light from a regeneratively amplified femtosecond Ti:sapphire laser (Spectra-Physics) at room temperature. The typical pulse width and repetition rate are 120 fs and 1 kHz, respectively. The laser beam is focused through a lens (focal length: 200 mm) to the interior of the samples that were placed on an XYZ stage.

x-ray diffraction (XRD) measurements were carried out to examine the crystallization, and the sample was prepared by evaporating the sample on a glass substrate. The absorption spectra were recorded on a Jasco V-570 UV/Vis/NIR Spectro-photometer (JASCO). Transmission–electron microscopy (TEM) observations were performed on a JEM-2010 electron microscope (JEOL). The sample was prepared by evaporating a drop of the sample on a copper grid coated with a carbon film.

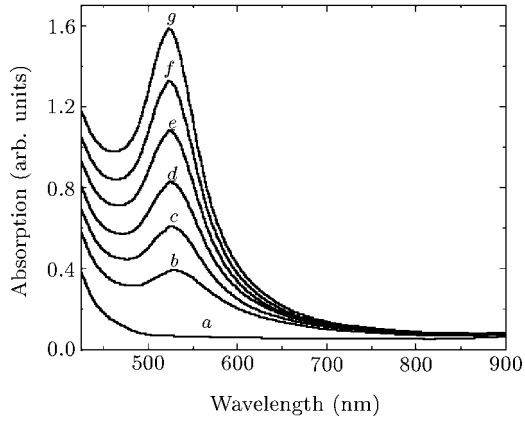

Fig. 1. Absorption spectra of $HAuCl_4$ solutions before and after different irradiation durations: (*a*) 0 min, (*b*) 5 min, (*c*) 10 min, (*d*) 15 min, (*e*) 20 min, (*f*) 25 min, and (*g*) 30 min.

Figure 1 shows the absorption spectra of the sample Au colloid with proceeding laser irradiation. It is observed that after the solution was irradiated, surface plasmon resonance absorption band appeared around 526 nm, which is the characteristic of Au nanoparticles.[6−8] Along with the irradiation time, the absorption peaks around 526 nm become predominant, indicating an increase in the number of Au nanoparticles. Furthermore, the peak position is blueshifted from the 530 nm after 5 min irradiation to 524 nm after 20 min irradiation, which means that the sizes becomes smaller with the irradiation time, but the effect of further laser irradiation is little. On the

other hand, the colour of $HAuCl_4$ solution under focused laser light irradiation changes from yellow to wine-red, suggesting the formation of Au colloid.

Figure 2 presents a transmission–electron microscopy (TEM) photograph of Au nanoparticles of the sample solution after 30-min laser irradiation. In the figure, well-separated black particles are seen clearly. These particles should be metallic Au, because they were not seen in the same $AuCl_4^-$ solution untreated by laser irradiation. Energy dispersive spectroscopy (EDS) analysis of the particles confirmed existence of gold content.

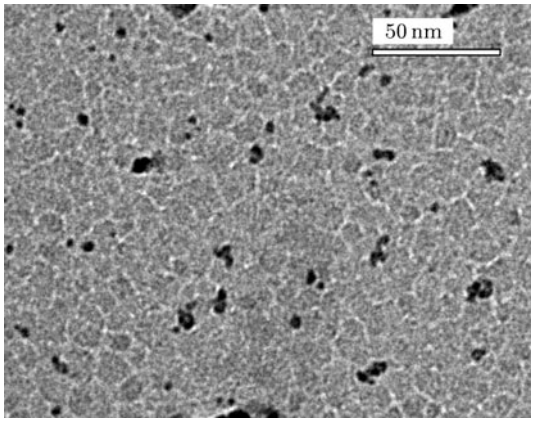

Fig. 2. TEM photograph of Au colloid prepared by irradiation with a 0.36-mJ pulse for 30 min.

Figure 3 shows the XRD patterns of the film for the $HAuCl_4$ aqueous solution after 30-min irradiation. In the XRD patterns, the broad peak around $2\theta = 24^\circ$ is due to the typical amorphous halo patterns of the glass substrate. However, according to the JCPDS reference (01–1172) the peaks $2\theta = 38.3^\circ$ and $2\theta = 44.3^\circ$ can be assigned to (111) and (200) reflection lines of cubic Au, indicating the formation of metallic Au, respectively. The size of Au nanoparticles was determined using Scherrer equation:

$$d = \frac{0.9\lambda}{\beta \cos\theta}, \qquad (1)$$

where λ is the wavelength of the x-ray source and β (radians) the full width at half maximum (FWHM) of the x-ray diffraction peak at the diffraction angle θ. The diameter of the Au nanoparticles was calculated by using the line broadening of the diffraction band at $2\theta = 38.3^\circ$ to be about 16 nm.

The nonlinear optical properties of the Au colloid placed in quartz cell of 1-mm thickness was measured by using a Z-scan experimental set-up,[9] with a frequency-doubled Q-switched mode-locked ns/ps Nd:YAG laser (Continuum), which produces 8-ns laser pulses at 532 nm with a repetition rate of 1 Hz. The linear transmittance of the sample is 40% at 532 nm.

The open aperture Z-scan experimental result for the sample is shown in Fig. 4, in which we can observe the smooth and symmetric valley-shaped curve. In the figure, a valley flanked by two unusual humps appears, which is consistent with the cases for Au nanoparticles dispersed in glass and induced by a femtosecond laser irradiation.[10] This phenomenon is attributed to the transition between the saturable absorption (SA) and reverse saturable absorption (RSA).

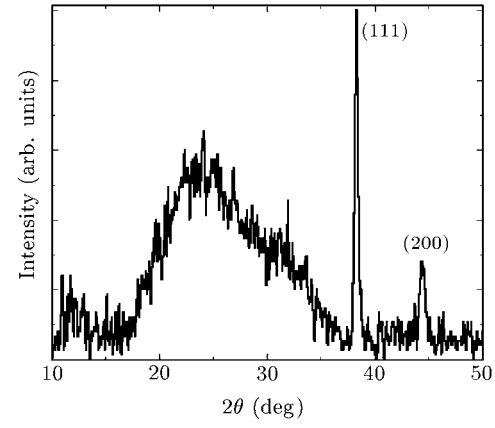

Fig. 3. x-ray diffraction pattern (Cu, K_α) for Au colloid prepared by irradiation with 0.36-mJ pulse for 30 min.

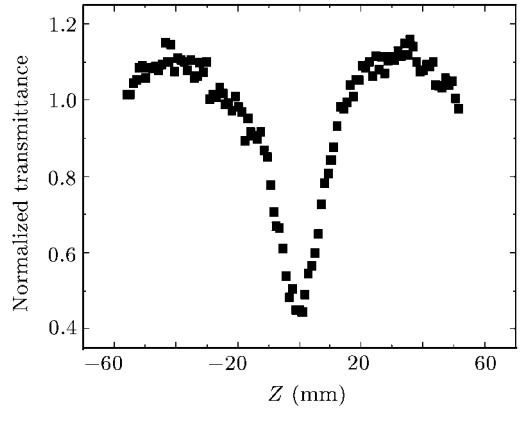

Fig. 4. Experimental result of the Z-scan data without an aperture for the Au colloid.

As shown in Fig. 1, a surface plasma resonance (SPR) peak resulting from the transition of the free electrons in the conduction band of metal nanoparticles appears around 526 nm for Au colloid. When the electrons in the ground-state are excited by a pulse close to absorption peak, they become free carries possessing a whole spectrum of energies. This will cause the ground-state plasma band to bleach or reduce in intensity, which is almost synchronous with the primary photon absorption. Then, some excited electrons will be pumped to the even higher energy level and cause excited-state absorption, and previous studies have shown the further excitation of the hot electrons around SPR peaks.[11–14] On the other hand, the rest excited electrons will relax to

the ground-state through electron–electron, electron-phonon, and phonon- phonon interactions within about 100 ps.[15,16] Thus, the broadband transient absorption subsides in this duration and gives way to the complete recovery of the bleached spectrum. The Z-scan results arise from the bleaching of the ground-state plasmon band prior to free-carrier absorption, which leads to a transition from saturable absorption (SA) to reverse saturable absorption (RSA). Therefore, for the Z-scan results without an aperture as shown in Fig. 4, moving the sample towards the focus, the increased laser intensity induces ground-state plasma to a bleach or reduction in intensity which results in a transmittance increase (SA process). While the sample is near the focus, the high laser intensity leads to the free carrier absorption dominating in this region, and thus, to acute decrease of the transmittance (RSA process). Such transmittance variation from increase first to decrease then will form local humps in the open aperture Z-scan curve.

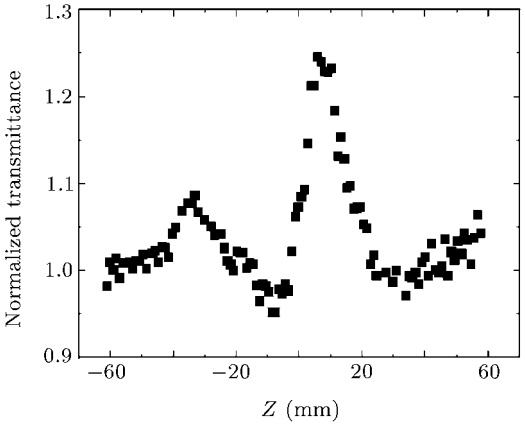

Fig. 5. Experimental result of the Z-scan data with an aperture divided by that without an aperture for the Au colloid.

The closed aperture (linear transmission of $S = 0.1$) Z-scan measurement was also performed for the investigation of nonlinear refraction. Figure 5 gives the result of the closed aperture Z-scan data divided by those of the open aperture, which also reveals an unusual peak-valley-peak-valley type curve. It can be explained as follows: (1) As moving the sample to the focus, the electrons excited by moderate laser intensity relax to the ground-state after the plasmon band bleaches through the electron–photon coupling with a nonradiative process. Thus the irradiated region is heated up, leading to a reduction of the local refractive index and resulting in the self-defocusing. (2) As the sample is close to the focus, the higher laser intensity further induces free carrier absorption. The oscillated electrons in higher energy levels give rise to an increase of the refractive index, resulting in the self-focusing. The intensity-dependent nonlinear refraction mentioned above is expected to have potential applications in optical information proceeding. Therefore, the nonlinear performances arise from the bleaching of the ground-state plasmon band prior to free-carrier absorption, which leads to a transition from saturable absorption (SA) to reverse saturable absorption (RSA), and a transition from self-defocusing to self-focusing when excited close to SPR peaks.

In addition, a theoretical modelling for the nonlinear absorptive and refractive characteristics was proposed in our previous study.[10] The transition behaviour from self-defocusing to self-focusing and from saturable absorption (SA) to reverse saturable absorption (RSA) depends on the surround medium size of Au nanoparticles,[5,10,17] since the properties were not observed for the Au nanoparticles protected by either C_{60}-tpy or C_{60}-bpy.

In summary, Au colloid has been prepared in $HAuCl_4$ aqueous solution induced by a near-infrared femtosecond laser. The size of the Au nanoparticles is less than 20 nm. The Au colloid sample reveals the transition characteristics both from SA to RSA and from self-defocusing to self-focusing.

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